Dr. Georg Mermigidis
Rotkreuzstrasse 4
D-73479 Ellwangen/Jagst
Germany
Tel. 00497961/7751

Katerini, 23 March 2001

Vacation address:
Agiou Dimitriou 72
GR-60100 Katerini
Greece
Tel./Fax: 0030351/35609

Assistant Commissioner for Patents
Box PCT
Washington D.C. 20231
United States of America

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Electrode and photoelectrochemical cell with four layers, method for producing a printable paste containing an electrolyte and/or carbon, and electrode

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The invention refers to a procedure for manufacturing an electrolyte and/or carbon containing printable paste, in particular as electrode material for a photoelectrochemical cell, a procedure for manufacturing an electrode, in particular an electrolyte containing counterelectrode of a photoelectrochemical cell, as well as to an electrolyte containing electrode and a photoelectrochemical cell.

Dye sensitized photoelectrochemical cells are well known, which do have as a semiconductor a material with a very large energy gap, like titanium dioxide. A characteristic of such a semiconductor with a large gap is that it absorbs in particular the low energy part of the sunlight to a smaller extent. The sensitivity of such photoelectrochemical cells is increased by a dye layer, which is applied to the semiconductor layer.

The functions of light absorption and charge carrier separation, which take place in the case of conventional solar cells, like for example silicon solar cells, in only one material, are separated in such dye sensitized cells. The light absorption takes place essentially in the dye sensitized layer, also called as chromophore layer, while the charge carrier separation takes place at the boundary layer semiconductor/dye.

As dye for the sensitized layer a ruthenium (Ru) containing dye is preferred.

Suitable electrolytes for such photoelectrochemical cells are for example iodide, bromide, hydrochinon or other redox systems.

As electrode usually metal oxide semiconductors are used, in particular titanium oxide. A photoelectrochemical cell, as it is described above, is for example well known from the EP 0584307 B1.

Counter electrodes of carbon have been proved to be particularly favourable for photoelectrochemical cells. To get such counter electrodes carbon pastes are manufactured, which are applied to the appropriate substrate, for example TCO glass, and then annealed or burned, in order to get a stable layer.

The light absorbing layer, usually a TiO_2-layer, can be sensitized only after burning or annealing the carbon paste, since the dye is temperature sensitive, and would therefore be destroyed in the process of burning or annealing. This has the consequence that for the sensitization much dye material is needed.

Therefore the purpose of the invention presented here is to make available an improved procedure for the production of a photoelectrochemical cell with a counterelectrode of carbon, as well as for the production of the material necessary for it and of an appropriate electrode and of a photoelectrochemical cell.

This purpose is reached with the procedures in accordance with the patent claim 1 as well as with an electrode in accordance with claim 3 and a photoelectrochemical cell in accordance with claim 6. The patent claims 2, 4 to 5, 7 to 9 and 10 represent particularly favourable features and kinds of realization.

According to the procedure of the invention presented here for manufacturing an electrolyte and/or a carbon containing printable paste, in particular as a electrode material for a photoelectrochemical cell, a solvent is supplied, which is mixed with electrolyte salts and electrolyte auxiliary.

1 to 30 weight % of carbon black with a large surface and/or conductivity carbon black and 1 to 30 weight % of graphite with very small electrical resistance are added to the solvent. The portion of weight depends on the electrolytic components used in each single case.

On principle the carbon containing paste can be manufactured on base of all suitable and also so far used electrolytes for the photoelectrochemical cell. Basically the carbon black or the graphite will not be in a functional interaction with the electrolytic components. Thus the invention is also applicable with electrolytes, which still can be developed in the future.

Thereupon the received suspension is agitated, in order to receive an essentially homogeneous distribution. Finally, the homogenized suspension is treated with ultrasound, so that a printable rigid paste develops.

The pastes can be characterized by impedance measurements.

Thus for the acquisition of necessary stiffness and printability of the paste according to the invention carbon is used that has a high agglomeration ability and a highly organized structure (fir tree), a large microscopic surface and a surface weight relation greater than 20 m^2/g, here called carbon black. As conductivity carbon black such carbon black is used that has a very high electrical conductivity, resistance values of max. $10^{-4}\ \Omega$ are acceptable.

Thus to decrease the electrical resistance of the paste according to the invention a type of carbon is used that has a small agglomeration ability and a low degree of structure (wooden peg), a small microscopic surface, but however a very small resistance in one direction, here called graphite. The resistance of the used graphite lies in the order of magnitude of $10^{-4}\ \Omega$, or less.

According to the invention's procedure, a printable rigid paste is made available, which has a consistency, which makes possible the application of the paste as an electrode or electrolyte respectively in a photoelectrochemical cell. In this procedure no burning or annealing is necessary. Therefore a thermal destruction of the dye is impossible, and the light absorbing layer can directly be sensitized with a dye layer. In that way the high loss of dye, which occurs due to the absorbing characteristics of carbon by using carbon electrodes, is avoided, so that for the sensitization less dye must be used, which leads to a clear reduction of costs.

It is further favourable that the quantity of electrolyte salt can be reduced. It was shown that a reduction down to 40 weight % of the original quantity in the pure electrolyte affects favourably the firmness of the paste.

Preferentially in the solvent the concentrations of the electrolyte salts and electrolyte auxiliary are in each case equal to those as they are used for the photoelectrochemical cell, in particular for the electrolytes in the solvent in a photoelectrochemical cell. As solvent in particular y-Butyrolactone is used.

It proves to be favourable when about 10 weight % of carbon black with a large surface and/or of a conductivity carbon black are added. Likewise it proves to be favourable that about 8 weight % of graphite with a very small electrical resistance are added. Thus particularly high efficiencies of the photoelectrochemical cell can be obtained.

As carbon black with a large microscopic surface in particular Degussa carbon black F.W. 200 is suitable, as conductivity carbon black in particular Degussa carbon black XE2 is suitable. As graphite with a very small electrical resistance preferentially Timcal Timrex SFG 44 or Timcal Timrex SFG 75 is used.

In order to produce an essentially homogeneous suspension, the suspension with the added particles is preferentially stirred for 5 minutes and then treated in the ultrasound bath for 15 minutes with ultrasound. The length of the treatment with ultrasound depends on the irradiated performance and has to be executed so long until the paste indicates the desired consistency. The paste should not indicate fluidity and should be exclusively easily spread.

With a particularly preferred procedure ultrasound is irradiated with a power density of approximately 1 W/cm^3 on a paste with a volume of 20 cm^3 during a period of 15 minutes.

With the procedure according to the invention for manufacturing an electrode, in particular an electrolyte containing electrode of a photoelectrochemical cell, an electrolyte and/or a carbon containing, printable paste are supplied. The paste is applied and adapted to a substrate or a substrate network.

For the production of a photoelectrochemical cell the paste is directly applied to the porous light reflecting insulator layer, which covers the light absorbing layer which was sensitized with a dye layer, which is located on an electrode of the photoelectrochemical cell.

After applying the paste to and pressing the paste on the substrate the layer already has its operational status. Burning or annealing the layer, in order to get a fixed consistency, is not necessary, so that a very fast and thus economical procedure for the manufacturing of an electrolyte containing electrode is supplied.

Preferably, to the applied and pressed paste furthermore a graphite layer is applied, in particular by dusting on. Thus a thin, very conductive layer is made available. The graphite layer must be covering, so that a horizontal conductivity is given. One or two layers of graphite particles are sufficient. The thickness of the layer therefore depends on the particle size of the graphite particles, and in addition on the used method of dusting the graphite.

An electrolyte containing electrode according to the invention is used in particular as a electrolyte counterelectrode of a photoelectrochemical cell and comprises an electrolyte and/or carbon containing printable paste. This layer, which exists of the electrolyte and/or carbon containing paste, can be covered on one side with a further layer of dusted graphite. The electrolyte containing electrode is preferentially

manufactured in the same way as it is described above, the analogue applies to the electrolyte and/or carbon containing printable paste. The electrode can essentially completely be produced at ambient temperature, neither annealing or burning nor the following troublesome bubble free filling up with dye and electrolyte is necessary in connection with the application in a photoelectrochemical cell, so that the production process is substantially simplified and reduced in price.

The electrolyte containing electrode shows comparable quality characteristics with regard to conventional electrodes, so that no or only a very small performance or efficiency loss has to be expected with the application of the electrolyte containing electrode according to the invention in photoelectrochemical cells. The thickness of the electrode can be adapted to the desired aims, applied in photoelectrochemical cells the usual thickness lies between 10 to 100 μm, preferentially at 20 μm.

The electrode arrangement consists preferentially of a conductive layer and/or an insulating layer, the conductive layer can serve as an additional electrode item, while the insulating layer can be a shielding for the electrode arrangement or the photoelectrochemical cell.

An electrode, a diaphragm as isolation layer, an electrolyte counterelectrode and a with a dye layer sensitized light absorbing layer constitute a photoelectrochemical cell which according to the invention contains a counterelectrode and an electrolyte, which are realized in an integral manner and do consist of a layer of electrolyte and/or carbon containing printable paste. The carbon containing, printable paste is in particular manufactured in a procedure, as it is described above.

Such a photoelectrochemical cell has to be manufactured easily and inexpensive, without having to accept crucial losses of performance data, in particular a reduced efficiency of the photoelectrochemical cell, in comparison with conventional cells. The cost use value of a cell according to the invention is crucially improved by the electrolyte containing counterelectrode in relation to the state of the art.

A particularly favourable photoelectrochemical cell has an additional graphite layer on the carbon containing paste, which was dusted. Furthermore the electrode and/or the combination of counterelectrode and electrolyte are additionally covered with an electrically conducting layer. This electrically conducting layer can serve as electrode item and supply a particularly efficient electrode arrangement.

Preferred is the photoelectrochemical cell, in particular this one which has at least one electrically leading layer, which is covered with at least one insulating layer, which seal off the photoelectrochemical cell with respect to outward.

As a dye for the sensitized dye layer preferentially a ruthenium (Ru) containing dye is used. As a material for the conductive layers a metal, ITO or an electrically conductive glass turned out to be favourable.

The features and advantages according to the invention become particularly clear with the only attached figure (figure 1).

Figure 1 schematically shows a possible layer structure of an execution form of a photoelectrochemical cell according to the invention, in which an execution form of an electrolyte containing counterelectrode according to the invention is integrated.

In figure 1 a preferential execution form of the cell according to the invention cell 1 is represented. It has to be pointed out expressively that the shown layer thickness are represented not true to scale, and do only serve as explanation and representation of the principles of the structure.

With the photoelectrochemical four layer cell according to the invention, whose production is essentially characterised by four simple process steps, the individual layers are assembled as follows:

The first layer, the light absorbing layer (40), here titanium dioxide TiO_2, which is applied to a electrically conductive carrier (10), here Indium Tin Oxide (ITO), is treated in a usual way with tertiary Butylpyridine or another Pyridinederivative. The TiO_2 - layer is porous and has a rough surface, to which a dye layer (50), also called as chromophore layer, is applied. In this implementation as dye a ruthenium containing dye is used. The combination of the TiO_2 - layer (40) and the dye layer (50) as described above are designated as light absorbing layer.

The second layer of the four layer cell consists of a light reflecting electrical insulation layer (80), which is applied to the light absorbing layer (40, 50) which is sensitized with a dye layer.

The third layer of the four layer cell, the electrode electrolyte combination layer (30) which consists of the electrolyte and/or carbon containing printable paste is directly printed onto the second layer and is pressed afterwards with a stamp into the insulation layer (80), with a pressure from approximately 100 to 50000 Pa (1 to 500 g/cm^2) in order to get thin layers. The paste (30) has a portion of 10 weight % Degussa carbon black F.W. 200 and a portion of 8 weight % graphite Timcal Timrex SFG 44. The paste is stirred for five minutes and then treated for 15 minutes with ultrasound before it is applied to the second layer, which is on the light absorbing layer (40, 50).

The fourth layer (31) of the four layer cell is a thin layer which consists itself of a few plies of graphite and which is made by dusting graphite onto the third layer, which comprises the electrolyte and/or carbon containing, printable paste (30).

The realisation of the four layer cell as shown in figure 1 contains an additional an ITO layer as electrical conductor (20).

The described photoelectrochemical cell is sealed off at both surfaces by an isolating layer (60) and (70) respectively. The isolating layers consist preferentially of a transparent material, like plastic or glass.

At least one of the isolating layers (60) and (70) must be permeable for the light, which has to be converted into electricity, so that the light can reach the light absorbing layer (40, 50).

In the implementation of a photoelectrochemical cell shown in figure 1 the insulating layer (60) is made of plastic, which is transparent for the light and is turned to the light, which has to be changed into electricity, and the insulating layer (70) is made of non-transparent plastic.

All the features of the invention that are revealed in the description above and in the drawing (figure 1) as well as in the requirements formulated before are both individually and in any combination substantial for the implementation of the invention.